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(54) HARD FILM

(57) Abstract:

PROBLEM TO BE SOLVED: To prepare a hard film superior in wear resistance to an (AI, Ti) (N, C) type film, which has the most excellent wear resistance among the conventional TiN film, TiC film, TiCN film, and (Al, Ti) (N, C) type film, and having wear resistance capable of meeting the demand for high speed cutting. SOLUTION: This hard film has a composition represented by (All-yXy)Z, where X and Z mean one element among Cr, V, and Mg and one element among N, C, B, Cn, BN, and CBN, respectively, and $0 \le y \le 0.3$ is satisfied.

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CLAIMS

[Claim(s)]

[Claim 1] It consists of the compound nitride, the compound carbide, the compound boride, the compound charcoal nitride, the compound **** nitride, the compound charcoal boride, or compound **** boride of aluminum and X (a kind of X:Cr, and V and Mg), and the composition (aluminum1-yXy) of aluminum and X

However, the hard anodic oxidation coatings characterized by consisting of composition shown by kind 0<y<=0.3 of X:Cr, and V and Mg.

[Claim 2] a thickness -- 0.1-20 micrometers it is -- hard anodic oxidation coatings according to claim 1

[Claim 3] The hard anodic oxidation coatings according to claim 1 or 2 formed in the front face of a cemented carbide or a high speed tool steel.

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DETAILED DESCRIPTION

[Detailed Description of the Invention] [0001]

[The technical field to which invention belongs] this invention belongs to the technical field about a hard anodic oxidation coatings suitable as a wear-resistant tool metallurgy type hard anodic oxidation coatings especially used for a manipulation of **, a cutting, a piercing, etc. about the hard anodic oxidation coatings excellent in abrasion resistance in detail about a hard anodic oxidation coatings. [0002]

[Description of the Prior Art] When manufacturing wear-resistant members, such as a cemented carbide (WC-Co system sintered alloy) or a high speed tool steel, forming the wear-resistant coat which becomes the base-material front face of these members from a metaled nitride and metaled carbide is performed for the purpose of having excelled performances, such as abrasion resistance, more.

[0003] As such a wear-resistant coat, it is TiN. Coat TiC coat is used widely and it is formed by the ion-plating method. The endurance with this higher TiN TiC coat is shown. Coat It is TiN if TiC coat is compared. Coat It is TiC, although TiC coat is excelled in thermal resistance (elevated-temperature oxidation resistance) and the function protected from the crater of the tool rake face which carries out a temperature up with the temperature increase by plastic working and frictional heat at the time of cutting is demonstrated. Compared with a coat, since it is a low degree of hardness, to the flank wear generated in the flank which touches **-ed material, rather, it is brittle and a flank wear is Then, recently [both], the hard anodic oxidation coatings of TiCN which suppresses a crater and a flank wear is put in practical use.

[0004] By the way, in connection with the laborsaving, energy saving, and the enhancement in a productivity in a cutting process, much more improvement in the speed of a cutting speed is demanded, and it is in the status that deep cuts of a high slitting or high delivery are performed in recent years. Thus, since a cutting conditions is in the inclination more made severe, it is the above TiN. A coat and TiC It has become impossible that it can finish responding to this request in a coat and TiCN coat. Namely, TiN A coat and TiC When the cutting tool which has a coat or TiCN coat performs a high speed cutting, when Ti in a coat oxidizes at an elevated temperature, a coat deteriorates and wear is very intense.

[0005] Then, it is TiN as a hard anodic oxidation coatings which was more excellent in abrasion resistance. TiC To TiCN, or Ti, N and C To add the 3rd of an except and the 4th element is tried. The compound nitride of Ti and aluminum which adds aluminum as the element [(aluminum, Ti)N], The hard anodic oxidation coatings (henceforth, these are named generically and it is called a system (N (aluminum, Ti), C) coat) which consists of compound carbide [(aluminum, Ti)C] or compound charcoal nitride [(aluminum, Ti) (N, C)] is proposed (JP,4-53642,B, JP,5-67705,B). In order to improve thermal resistance (elevated-temperature oxidation resistance) and a degree of hardness, aluminum is added, aluminum oxidizes alternatively at an elevated temperature, this (aluminum, Ti) (N, C) system coat turns into a protective film, and prevents oxidization of the coat under this coat, and, thereby, its thermal resistance is improving. However, it is TiN at 800 ** grade. A coat deteriorates like the case of a coat, therefore it is unsuitable to the high speed cutting said that edge-of-a-blade temperature becomes 1000 degrees C or more, and cannot correspond to it, but the hard anodic

oxidation coatings to which it has improved the performance (especially abrasion resistance) further since the degree of hardness of a coat is not not much high, either, about 2500 Hv and is needed.

[Problem(s) to be Solved by the Invention] For this invention, it is made paying attention to such a situation, and the purpose is the aforementioned conventional TiN. A coat and TiC The trouble in a coat, TiCN coat, and a system (N (aluminum, Ti), C) coat tends to be canceled, and it is going to offer the hard anodic oxidation coatings which excelled the system coat which is most excellent in abrasion resistance in the coat of these former (N, C) (aluminum, Ti) in abrasion resistance.

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the hard anodic oxidation coatings concerning this invention is used as the hard anodic oxidation coatings according to claim 1 to 3, and it is taken as the following configurations.

[0008] That is, a hard anodic oxidation coatings according to claim 1 consists of the compound nitride, the compound carbide, the compound boride, the compound charcoal nitride, the compound **** nitride, the compound charcoal boride, or compound **** boride of aluminum and X (a kind of X:Cr, and V and Mg), and the composition (aluminum1-yXy) of aluminum and X

However, it is the hard anodic oxidation coatings characterized by consisting of composition shown by kind 0<y<=0.3 of X:Cr, and V and Mg.

[0009] a hard anodic oxidation coatings according to claim 2 -- a thickness -- 0.1-20 micrometers it is - it is a hard anodic oxidation coatings according to claim 1 A hard anodic oxidation coatings according to claim 3 is a hard anodic oxidation coatings according to claim 1 or 2 formed in the front face of a cemented carbide (WC-Co system sintered alloy) or a high speed tool steel.

[Embodiments of the Invention] The hard anodic oxidation coatings concerning this invention is obtained for example, by the sputtering method etc. This hard anodic oxidation coatings has the aforementioned **** composition, and is excellent in thermal resistance (elevated-temperature oxidation resistance), and excels the system coat the degree of hardness excels [coat] in abrasion resistance most in the conventional coat highly therefore (N, C) (aluminum, Ti) in abrasion resistance, and has the abrasion resistance which can correspond in the case of a high speed cutting. [0011] This detail is explained below.

[0012] It is supposed that the aforementioned conventional system (N (aluminum, Ti), C) coat proposed since it corresponds to deep cuts of much more improvement in the speed, a high slitting or high delivery of a cutting speed, etc., etc. has comparatively good abrasion resistance. It is thought that it is based on thermal resistance (elevated-temperature oxidation resistance) improving since the oxide film formed of alternative oxidization of aluminum turns into a protective film, and a degree of hardness rising as the ground. However, since it will be in the very hot status in the case of a high speed cutting, Ti also oxidizes, a coat deteriorates, the protection nature of a coat is lost, and wear becomes intense, then, the thing which eliminated Ti -- namely, -- AlN coat and AlC Although it will be thought that it is good if it is made a coat and AlCN coat (these are named generically and it is henceforth called aluminum (N, C) system coat) AlN aluminum of a grade (N, C) As a hard anodic oxidation coatings used for a tool, it is soft, and crystal system is usually hexagonal system, therefore a degree of hardness is as low as about 1000 Hv, and it is [a system coat has very low abrasion resistance, and] inadequate.

[0013] then, AlN etc. -- aluminum (N, C) As a result of adding various elements and evaluating a coat performance, thermal resistance (elevated-temperature oxidation resistance) and a degree of hardness improve [therefore] by carrying out specified quantity inclusion of a kind (henceforth, X) of Cr, V, and Mg. Abrasion resistance can improve rather than the conventional system (N (aluminum, Ti), C) coat, it can have now the abrasion resistance which can correspond when it is a high speed cutting, and it turns out that it is good for X occupied in aluminum and X to carry out the content of this X comparatively, and to make it less than [30at%]. About the cause of the enhancement in the thermal resistance by addition of such X (namely, a kind of Cr, V, and Mg), and a degree of hardness the **** valence-electron distribution reported about the compound carbide [:(Ti, Nb) C] of Ti and Nb etc. although it is not clear, and relation (Su-rface and Coatings Technology and 33 (1987) 91-103) of a

degree of hardness It is thought that it is based on change of the crystal system to cubic system from hexagonal system.

[0014] this invention is made based on such knowledge, the hard anodic oxidation coatings concerning this invention consists of the compound nitride, the compound carbide, the compound boride, the compound charcoal nitride, the compound **** nitride, the compound charcoal boride, or compound **** boride of aluminum and X (a kind of X:Cr, and V and Mg) like the above, and the composition (aluminum1-yXy) of aluminum and X

However, it is made to consist of composition shown by kind 0<y<=0.3 of X:Cr, and V and Mg. [0015] The time of setting a kind of this hard anodic oxidation coatings, i.e., Cr, V, and Mg, to X (aluminum1-yXy) N, (aluminum1-yXy) the composition shown by C, B (aluminum1-yXy), CN (aluminum1-yXy), BN (aluminum1-yXy), or CBN (aluminum1-yXy) **** -- becoming -- 0< y<=0.3 it is -- it is characterized by things the composition this hard anodic oxidation coatings is indicated to be by Z (aluminum1-yXy) here when N, C, B, CN, BN, or CBN is set to Z **** -- becoming -- 0< y<=0.3 it is -- it is characterized by things In addition, it does not restrict that it is 1:1, but, also in the 1:abbreviation 1 (1 or less [near 1]), is contained, for example, :(aluminum1-yXy) Z also has the case of 1:0.90.

[0016] If it puts in another way, it is the hard anodic oxidation coatings characterized by the rate of X which consists of compound nitride, compound carbide, compound boride, compound charcoal nitride, compound **** nitride, compound charcoal boride, or compound **** boride [, i.e., (aluminum1-yXy), Z], of aluminum and X (however, a kind of X:Cr, and V and Mg), and is occupied in this aluminum and X being less than [30at%] (0% not being included).

[0017] Therefore, the hard anodic oxidation coatings concerning this invention is excellent in thermal resistance (elevated-temperature oxidation resistance) collating with the aforementioned knowledge, and excels the system coat the degree of hardness excels [coat] in abrasion resistance most in the conventional coat highly therefore (N, C) (aluminum, Ti) in abrasion resistance, and it turns out that it is what has the abrasion resistance which can correspond in the case of a high speed cutting.

[0018] It is y of the 30at% less than, i.e., (aluminum1-yXy), Z, excluding 0% in the rate of X occupied in aluminum and X here 0< y<=0.3 Carrying out It is y 0.3 If it super-**s, the component (namely, AlZ which carries out a postscript) concerning aluminum will decrease. It is because elevated-temperature oxidation resistance and a degree of hardness fall, abrasion resistance falls by that cause, and it becomes inadequate, and X will not contain, but it will become impossible to plan wear-resistant enhancement by X addition and abrasion resistance will become inadequate on the other hand, if y is set to 0.

[0019] In addition, for the aforementioned (aluminum1-yXy) Z, the amount of AlZ components will be lessened and it is y to enlarge y, since it can be expressed as the 1-y-(XZ) y solid solution if a solid-solution component describes (AlZ) 0.3 If it super-**s, the amount of AlZ components will decrease too much, and un-arranging [which it is called the above-mentioned **** abrasion resistance fall] arises. To it, making y small will make [many] the amount of AlZ components, as a result its abrasion resistance will improve such a point to 0 < y <= 0.3 ** -- although it is necessary to carry out, in order to improve abrasion resistance to an authenticity more -- 0 < y <= 0.2 ** -- carrying out is desirable, and it is so still good that y is close to 0 (however, 0 is removed) in respect of wear-resistant enhancement However, if y is made small too much, since the amount of XZ components will decrease too much, crystal system will change from cubic system to hexagonal system and abrasion resistance will become low, it is desirable to be referred to as 0.01 <=y from the point.

[0020] It is a thickness 0.1, when coating and using this hard anodic oxidation coatings for members, such as a tool by which wear-resistant and oxidation-resistant both are demanded, especially about the thickness of the hard anodic oxidation coatings concerning this invention, although not limited. mum Carrying out above is desirable. It is a thickness 0.1 if this hard anodic oxidation coatings is uniformly coated in oxidation resistance. mum Also for the following, an effect is the thickness 0.1 of a certain thing. mum It is because it seldom comes to demonstrate the wear-resistant grant effect and it may become inadequate [abrasion resistance] in the following. On the other hand, it is 20 micrometers of thicknesss. 20 micrometers since there are few wear-resistant and oxidation-resistant enhancement effects although a thickness is thickened in **, and coating time becomes long and a productivity falls

It is desirable to make it below (hard anodic oxidation coatings according to claim 2). [0021] Moreover, about especially the base material coated with the hard anodic oxidation coatings concerning this invention, although it cannot be limited, and various base materials can be used according to intended use or need, for example, it can form and use for various tool base-material front faces in the field of a tool, it is desirable to use a cemented carbide (WC-Co system sintered alloy) or a high speed tool steel (high speed steel) as a tool base material (hard anodic oxidation coatings according to claim 3). It is because this invention coat has very good adhesion to especially a cemented carbide and a high speed tool steel.

[0022] Coating on the base-material front face of the hard anodic oxidation coatings concerning this invention can be performed by the PVD represented by the ion-plating method which ionizes a metal component by the arc discharge which makes a cathode an evaporation source, the sputtering method or ion-implantation, etc. When the content of the arc ion-plating method is explained in these, it is the metal component ionized by the arc discharge which makes a cathode an evaporation source N2 and CH4 Or it is made to react in the ambient atmosphere of BF3 gas or those mixed gas, and the base-material front face which gave bias voltage is made to carry out a deposit. Although aluminum, Cr, aluminum and V, or aluminum and Mg may be individually used as a cathode, respectively at this time, it consists of the purpose composition itself. aluminum1-yXy There are a cathode (target), then an advantage that control of coat composition is easy. In this case, aluminum1-yXy A composition gap of the cathode matter (aluminum1-yXy) is hardly produced, but moreover, vaporization is performed in a high current region A [some dozens of] or more, therefore it is [an ionization efficiency is high, bias voltage to a base material.

[Example]

(Example 1) A cathode arc method ion plating system is used, and it is as the cathode electrode. The target of aluminum1-yXy (however, X: Cr, V or Mg, y: variously change) was attached, and, on the other hand, the tool chip made from a cemented carbide (WC-10%Co system sintered alloy) was attached in the substrate (base material) electrode holder of this equipment as a base material. Moreover, the substrate rolling mechanism and heater for securing the homogeneity of the coat formation status were formed in this equipment.

[0024] And after it impressed the bias voltage of -30V to the base material where the heating hold of the base material (chip) is carried out at 400 **, and introducing high-grade N2 gas, or N2 / CH4 mixed gas in equipment at the above-mentioned heater, it considers as the ambient atmosphere of 1x10-3Torr, and arc discharge is started, and it is 5 micrometers of thicknesss to a base-material front face. Membranes were formed. Thus, composition of the obtained coat is shown in Tables 1-2 (No.1-33, 36-68). In this, the thing of No.1-27, and 36-62 is a hard anodic oxidation coatings concerning the example of this invention, and No.28 -33, and 63-68 are the coats concerning the example of a

[0025] furthermore, a comparison sake -- cathode (target) aluminum1-yTiy or Ti -- using -- such a point -- removing -- the same equipment and same technique as the above -- N (aluminum, Ti) coat and TiN The coat was formed. Composition of these coats is shown in Tables 1-2 (No.34, 35, 69, and 70).

[0026] Thus, the cutting examination was performed on two kinds of conditions as follows using the tool chip by which coat formation was carried out. The test result is shown in Tables 1-2.

** **-ed material:S45C, cutting-speed:170m/, and min, and feed-rate:0.25mm/rev -- cutting deeply --: 1mm and **-ed [cutting-time:25 minute **] material --: SKD11, cutting-speed:150m/, and min, and feed-rate:0.2mm/rev -- cutting deeply --: 2mm and cutting-time: -- 25 minutes [0027] ****** also has very few amounts (width of face of a wear width-of-face:wear part) of flank wears, and face-wear depths, and the tool chip which has the coat which starts the example of this invention compared with the tool chip which has a coat concerning the example of a comparison excels [******] in abrasion resistance very much so that clearly from Tables 1-2.

[0028] (Example 2) the thickness of the coat which uses a platinum plate and is formed in a base-material front face as a base material in order to investigate the oxidation resistance of a coat -- 10

micrometers ** -- it carried out and the coat of the composition shown in Table 3 was formed except for these points by the same, same equipment and same, same technique as an example 1 In this, the thing of No.71 -76 is a hard anodic oxidation coatings concerning the example of this invention, and No.77 -84 are a coat concerning the example of a comparison.

[0029] Thus, about the platinum plate by which coat formation was carried out, in order to investigate the oxidation resistance of the coat, thermobalance equipment is used, and it is flow rate:150cc of temperature-up domain:room temperature -1200 degree-C, programming-rate:10 degrees C /, min, controlled-atmosphere:dry-air, and controlled atmosphere/min. The oxidation test was performed on conditions. And the temperature in the rapid point produced in a temperature-up process increasing [weight] was determined as oxidization start temperature, and it asked for it. The result is shown in Table 3. Moreover, the Vickers hardness (50g of loads) of a coat was measured. The result is written together and shown in Table 3.

[0030] the coat which starts the example of a comparison so that clearly from Table 3 -- TiN the coat which is about 600 ** and starts the example of this invention in a coat to oxidization starting by about 800 ** in N (aluminum, Ti) coat -- yes, oxidization start temperature of **** is high and it is excellent in elevated-temperature oxidation resistance [0031]

[Table 1]

No	皮膜の組成	被削材	逃げ面 摩耗幅 (mm)	すくい面 摩耗深さ (µm)	備考
1 2 3 4 5 6 7 8 9	(Alo. s. Cro. 1)N (Alo. s. Cro. 2)N (Alo. 7. Cro. 2)N (Alo. s. Cro. 2)B (Alo. s. Cro. 2)C (Alo. s. Cro. 2)NC (Alo. s. Cro. 2)NB (Alo. s. Cro. 2)BC (Alo. s. Cro. 2)NC	S45C	0. 05 0. 04 0. 05 0. 07 0. 06 0. 04 0. 07 0. 08	Ნ ᲡᲜ & ᡧᲡᲜ%%	
10 11 12 13 14 15 16 17 18	(Alo. s, Vo. 1)N (Alo. s, Vo. 2)N (Alo. 7, Vo. 3)N (Alo. s, Vo. 2)B (Alo. s, Vo. 2)C (Alo. s, Vo. 2)NC (Alo. s, Vo. 2)NC (Alo. s, Vo. 2)BC (Alo. s, Vo. 2)NCB	S45C	0. 06 0. 05 0. 07 0. 05 0. 05 0. 04 0. 04	767665874	本発明例
19 20 21 22 23 24 25 26 27	(Alo. s. Mgo. 1)N (Alo. s. Mgo. 2)N (Alo. 7. Mgo. 3)N (Alo. s. Mgo. 1)B (Alo. s. Mgo. 1)C (Alo. s. Mgo. 1)NC (Alo. s. Mgo. 1)NB (Alo. s. Mgo. 1)BC (Alo. s. Mgo. 1)NCB	S45C	0. 05 0. 06 0. 07 0. 08 0. 06 0. 05 0. 07 0. 06	6 7 8 9 8 5 6 7 4	
28 29 30 31 32 33	(Alo. 6, Cro. 4)N (Alo. 4, Cro. 6)N (Alo. 6, Vo. 4)N (Alo. 4, Vo. 6)N (Alo. 6, Mgo. 4)N (Alo. 4, Mgo. 6)N	S45C	0. 16 0. 17 0. 17 0. 18 0. 19 0. 20	1 9 2 1 2 2 2 3 2 5 2 6	比較例

34	Tin	S45C	0.	15	18	i i	ı
35	(Alo. s. Tio. 4)N	S45C	0.	1 0	1 2	比較例	

[0032] [Table 2]

<u> </u>	able 2]					
No	皮膜の組成	被削材	逃げ面 摩耗幅 (mm)	すくい面 摩耗深さ (µm)	備考	
36 37 38 39 40 41 42 43 44	(Alo. 8, Cro. 2)N (Alo. 7, Cro. 2)N (Alo. 8, Cro. 2)B (Alo. 8, Cro. 2)C (Alo. 8, Cro. 2)NC (Alo. 8, Cro. 2)NB (Alo. 8, Cro. 2)NB	SKD11	0. 3 0 0. 25 0. 3 0 0. 2 5 0. 2 0 0. 2 5 0. 1 5	8 7 8 9 8 6 7 9 7		
45 46 47 48 49 50 51 62 53	(Alo. 8, Vo. 2)N (Alo. 7, Vo. 2)N	SKD11	0. 3 0 0. 2 5 0. 3 0 0. 3 5 0. 2 0 0. 3 5 0. 2 5 0. 1 5	9 8 1 0 1 1 7 9 8 6	本発明例	
54 55 56 57 58 59 60 61 62	(Alo. 9. Mgo. 1)N (Alo. 8. Mgo. 2)N (Alo. 7. Mgo. 3)N (Alo. 9. Mgo. 1)B (Alo. 9. Mgo. 1)C (Alo. 9. Mgo. 1)NC (Alo. 9. Mgo. 1)NB (Alo. 9. Mgo. 1)BC (Alo. 9. Mgo. 1)NCB	SKD11	0. 20 0. 20 0. 35 0. 25 0. 25 0. 25 0. 20	8 9 1 0 9 9 7 8 9 6		
63 64 65 66 67 68	(Alo. 6. Cro. 4)N (Alo. 4. Cro. 5)N (Alo. 6. Vo. 4)N (Alo. 4. Vo. 5)N (Alo. 6. Mgo. 4)N (Alo. 4. Mgo. 6)N	SKD11	0. 65 0. 70 0. 70 0. 75 0. 80 0. 85	2 6 2 7 2 8 2 9 2 9 3 0	比較例	
69	TiN	SKD11	0.60	2 5	U-btm:	
70	(Al. Ti) N	SKD11	0.40	1 8	比較例	

[0033] [Table 3]

No	皮膜の組成	酸化開始 温度 (°C)	ビッカース 硬度 (Hv)	備考
71 72 73 74 75 76	(Alo. s. Cro. 2)N (Alo. s. Vo. 2)N (Alo. s. Mgo. 1)N (Alo. s. Cro. 2)NC (Alo. s. Vo. 2)NB (Alo. s. Mgo. 2)BC	1 0 5 0 1 0 0 0 1 0 0 0 9 5 0 9 0 0 9 0 0	3 2 0 0 3 0 0 0 2 8 0 0 3 5 0 0 3 1 0 0 3 2 0 0	本発明例
77 78 79 80 81 82	(Alo. 6, Cro. 4)N (Alo. 6, Vo. 4)N (Alo. 6, Mgo. 4)N (Alo. 6, Cro. 4)NC (Alo. 6, Vo. 4)NB (Alo. 6, Mgo. 4)BC	000000 0550000 766656	2 1 0 0 1 8 0 0 1 5 0 0 2 2 0 0 2 0 0 0 1 9 0 0	比較例
83	TiN	600	2000	比較例
84	(Al. Ti) N	800	2500	レレザメリアリ

[0034]

[Effect of the Invention] The hard anodic oxidation coatings concerning this invention is excellent in thermal resistance (elevated-temperature oxidation resistance), and its degree of hardness is high. The sake, The conventional TiN A coat and TiC The system coat which is most excellent in abrasion resistance in the coat, TiCN coat, and the system (N (aluminum, Ti), C) coat (N, C) (aluminum, Ti) is excelled in abrasion resistance. It has the abrasion resistance which can correspond in the case of a high speed cutting, therefore can use suitably as a hard anodic oxidation coatings of the tool base material for high speed cuttings. It can use suitably as a wear-resistant tool metallurgy type hard anodic oxidation coatings which can attain now much more improvement in the speed of a cutting speed, and is used for a manipulation of a piercing etc., and the effect that enhancement in the tool performance metallurgy type performance by those wear-resistant enhancements and enhancement in a life can be aimed at now is done so.

[Translation done.]

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FA) Follows a bar a			最終頁に続く

(54) 【発明の名称】 硬質皮膜

(57)【要約】

【特許請求の範囲】

【請求項1】 AIとX(X:Cr、V、Mgの一種)の複合 窒化物、複合炭化物、複合ホウ化物、複合炭窒化物、複 合ホウ窒化物、複合炭ホウ化物または複合炭窒ホウ化物 よりなり、そのAIとXの組成が、

 $(Al_{1-y}X_y)$

但し、X:Cr、V、Mgの一種

 $0 < y \le 0.3$

で示される組成からなることを特徴とする硬質皮膜。

【請求項2】 膜厚が0.1 ~20 µm である請求項1記載の硬質皮膜。

【請求項3】 超硬合金または高速度工具鋼の表面に形成された請求項1又は2記載の硬質皮膜。

【発明の詳細な説明】

[0001]

【発明の属する技術分野】本発明は、硬質皮膜に関し、 詳細には、耐摩耗性に優れた硬質皮膜に関し、特には、 切削加工、穿孔加工等の加工に使用される工具や金型の 耐摩耗性硬質皮膜として好適な硬質皮膜に関する技術分 野に属する。

[0002]

【従来の技術】超硬合金(WC-Co 系焼結合金)又は高速 度工具鋼等の耐摩耗性部材を製作する場合、耐摩耗性等 の性能をより優れたものとすることを目的として、それ ら部材の基材表面に金属の窒化物や炭化物よりなる耐摩 耗性皮膜を形成することが行われている。

【0003】かかる耐摩耗性皮膜としては、TiN皮膜やTiC皮膜が汎用され、それはイオンプレーティング法により形成されている。このTiN皮膜とTiC皮膜とを比較すると、TiN皮膜はTiC皮膜よりも耐熱性(高温耐酸化性)に優れており、切削時の加工熱や摩擦熱によって昇温する工具すくい面のクレータ摩耗から保護する機能を発揮するが、TiC皮膜に比べて低硬度であるため、被削材と接する逃げ面に発生するフランク摩耗に対してはむしろ脆弱であり、フランク摩耗に対しては TiC皮膜の方が高い耐久性を示す。そこで、最近ではクレータ摩耗とフランク摩耗を共に抑制するTiCNの硬質皮膜が実用化されている。

【0004】ところで、近年、切削工程の省力化や省エネルギー化及び生産性向上に伴い、切削速度の一層の高速化が要望されており、高切り込み或いは高送り等の重切削が行われる状況にある。このように切削条件がより過酷化する傾向にあるため、前記TiN皮膜、TiC皮膜、TiC皮膜ではこの要請に応えきれなくなっている。即ち、TiN皮膜、TiC皮膜又はTiCN皮膜を有する切削工具により高速切削を行った場合、高温で皮膜内のTiが酸化することにより、皮膜が劣化し、摩耗が非常に激しい。【0005】そこで、より耐摩耗性に優れた硬質皮膜として、TiNやTiC或いはTiCNにTi、N、C以外の第3、第4元素を添加することが試みられており、その元素と

してA1を添加したものであるところの、TiとA1の複合窒化物〔(A1,Ti)N〕、複合炭化物〔(A1,Ti)C〕或いは複合炭窒化物〔(A1,Ti)(N,C)〕よりなる硬質皮膜(以降、これらを総称して(A1,Ti)(N,C)系皮膜という)が提案されている(特公平4-53642号公報、特公平5-67705号公報)。この(A1,Ti)(N,C)系皮膜は、耐熱性(高温耐酸化性)及び硬度を向上するためにA1を添加したものであり、高温でA1が選択的に酸化し、保護皮膜となって該皮膜下の皮膜の酸化を防止し、それにより耐熱性が向上している。しかしながら、800℃程度でTiN皮膜の場合と同様に皮膜が劣化し、そのため、刃先温度が1000℃以上となるといわれる高速切削には不適であって対応できず、皮膜の硬度もHv2500程度とあまり高くはないため、更に性能(特に耐摩耗性)を改善した硬質皮膜が必要となっている。

[0006]

【発明が解決しようとする課題】本発明はかかる事情に着目してなされたものであって、その目的は前記従来のTiN 皮膜、TiC 皮膜、TiCN皮膜、(A1,Ti)(N,C)系皮膜での問題点を解消し、これら従来の皮膜の中で最も耐摩耗性に優れている(A1,Ti)(N,C)系皮膜よりも耐摩耗性に優れた硬質皮膜を提供しようとするものである。

[0007]

【課題を解決するための手段】上記目的を達成するために、本発明に係る硬質皮膜は請求項1~3記載の硬質皮膜としており、それは次のような構成としたものである。

【0008】即ち、請求項1記載の硬質皮膜は、AlとX(X: Cr、V、Mgの一種)の複合窒化物、複合炭化物、複合炭化物、複合炭窒化物、複合ホウ窒化物、複合炭窒化物、複合ホウ窒化物、複合炭ホウ化物または複合炭窒ホウ化物よりなり、そのAlとXの組成が、

 $(Al_{1-y}X_y)$

但し、X:Cr、V、Mgの一種

 $0 < y \le 0.3$

で示される組成からなることを特徴とする硬質皮膜である。

【0009】請求項2記載の硬質皮膜は、膜厚が0.1~20μmである請求項1記載の硬質皮膜である。請求項3記載の硬質皮膜は、超硬合金 (WC-Co 系焼結合金)または高速度工具鋼の表面に形成された請求項1又は2記載の硬質皮膜である。

[0010]

【発明の実施の形態】本発明に係る硬質皮膜は、例えばスパッタリング法等により得られる。この硬質皮膜は、前記の如き組成を有し、耐熱性(高温耐酸化性)に優れ、又、硬度が高く、そのため、従来の皮膜の中で最も耐摩耗性に優れている(AI,Ti)(N,C)系皮膜よりも耐摩耗性に優れ、高速切削の場合に対応可能な耐摩耗性を有する。

【0011】この詳細を以下説明する。

【0012】切削速度の一層の高速化や高切り込み或いは高送り等の重切削に対応するために提案されている前記従来の(Al,Ti)(N,C)系皮膜は、耐摩耗性が比較的良いとされている。その理由としては、Alの選択的酸化により形成された酸化皮膜が保護皮膜となるために耐熱性(高温耐酸化性)が向上し、又、硬度も上昇することによるものと考えられている。しかし、高速切削の場合は極めて高温の状態となるため、Tiも酸化してしまい、皮膜が劣化し、皮膜の保護性を失って摩耗が激しくなる。そこで、Tiを排除したもの、即ち AlN皮膜、AlC 皮膜、AlCN皮膜(以降、これらを総称して Al(N,C)系皮膜という)にするとよいと考えられるが、AlN 等のAl(N,C)系皮膜は通常結晶系が六方晶系であり、そのため硬度がHv1000程度と低く、工具に用いる硬質皮膜として軟らかく、耐摩耗性が非常に低くて不充分である。

【0013】そこで、AIN等のAI(N,C)に様々な元素を添加し、皮膜性能を評価した結果、Cr、V、Mgの一種(以降、X)を所定量含有することにより、耐熱性(高温耐酸化性)及び硬度が向上し、そのため、従来の(AI,Ti)(N,C)系皮膜よりも耐摩耗性が向上し、高速切削の場合に対応可能な耐摩耗性を有することができるようになり、そして、このXの含有量はAI及びX中に占めるXの割合として30at%以下にするとよいことがわかった。このようなX(即ちCr、V、Mgの一種)の添加による耐熱性及び硬度の向上の原因については、明らかではないが、TiとNbの複合炭化物〔:(Ti,Nb)C〕等について報告されている如き価電子分布と硬度の関係(Su-rface and Coatings Technology, 33 (1987) 91-103)や、六方晶系から立方晶系への結晶系の変化によるものと考えられる。

【0014】本発明はかかる知見に基づきなされたものであり、本発明に係る硬質皮膜は、前記の如く、A1とX(X:Cr、V、Mgの一種)の複合窒化物、複合炭化物、複合ホウ化物、複合炭窒化物、複合ホウ窒化物、複合炭ホウ化物または複合炭窒ホウ化物よりなり、そのA1とXの組成が、

 $(Al_{1-y}X_y)$

但し、X:Cr、V、Mgの一種

 $0 < y \le 0.3$

で示される組成からなるようにしている。

であるとは限らず、1:約1(1に近い1以下) の場合も含まれ、例えば1:0.90の場合もある。

【0016】換言すれば、AIとX(但し、X:Cr、V、Mgの一種)の複合窒化物、複合炭化物、複合炭化物、複合ホウ化物、複合炭窒化物、複合ホウ窒化物、複合炭ポウ化物または複合炭窒ホウ化物〔即ち(AI_{1-y}X_y) Z〕よりなり、このAI及びX中に占めるXの割合が30at%以下(0%を含まず)であることを特徴とする硬質皮膜である。

【0017】従って、本発明に係る硬質皮膜は、前記知見と照合するに、耐熱性(高温耐酸化性)に優れ、又、硬度が高く、そのため、従来の皮膜の中で最も耐摩耗性に優れている(A1,Ti)(N,C)系皮膜よりも耐摩耗性に優れ、高速切削の場合に対応可能な耐摩耗性を有するものであることがわかる。

【0019】尚、前記($Al_{1-y}X_y$) Zは固溶体成分で記述すれば (AlZ) $_{1-y}$ - (XZ) $_y$ 固溶体と表現できるので、yを大きくすることはAlZ成分量を少なくすることになり、yを0.3 超とするとAlZ成分量が少なくなり過ぎ、上記の如き耐摩耗性低下という不都合が生じるのである。それに対し、yを小さくすることはAlZ成分量を多くすることになり、ひいては耐摩耗性が向上することになる。かかる点から、 $0 < y \le 0.3$ とする必要があるが、耐摩耗性をより確実に向上するためには $0 < y \le 0.2$ とすることが望ましく、更にはyは0(但し0を除く)に近いほど耐摩耗性の向上面ではよい。しかし、yを小さくし過ぎると、XZ成分量が少なくなり過ぎ、結晶系が立方晶系から六方晶系へと変わり耐摩耗性が低くなるので、その点からは $0.01 \le y$ とすることが望ましい。

【0020】本発明に係る硬質皮膜の膜厚については、特に限定されるものではないが、耐摩耗性及び耐酸化性の両方が要求される工具等の部材に該硬質皮膜をコーティングして用いる場合は、膜厚 $0.1~\mu m$ 以上にすることが望ましい。それは、耐酸化性においては該硬質皮膜が均一にコーティングされれば膜厚 $0.1~\mu m$ 未満でも効果はあるものの、膜厚 $0.1~\mu m$ 未満では耐摩耗性付与効果があまり発揮されなくなり、耐摩耗性が不充分となる可能性があるからである。一方、膜厚 $20~\mu m$ 超では膜厚を厚くする割りには耐摩耗性及び耐酸化性の向上効果が少なく、又、コーティング時間が長くなって生産性が低下することから、 $20~\mu m$ 以下にすることが望ましい(請求項2記載の硬質皮膜)。

【0021】又、本発明に係る硬質皮膜がコーティングされる基材については、特に限定されるものではなく、用途や必要性に応じて種々の基材を使用でき、例えば工具の分野において種々の工具基材表面に形成して用いることができるが、工具基材としては超硬合金(WC-Co系焼結合金)または高速度工具鋼(ハイス)を用いることが望ましい(請求項3記載の硬質皮膜)。それは、本発明皮膜は特に超硬合金及び高速度工具鋼に対して密着性が非常によいからである。

【0022】本発明に係る硬質皮膜の基材表面へのコー ティングは、カソードを蒸発源とするアーク放電によっ て金属成分をイオン化するイオンプレーティング法やス パッタリング法、或いはイオン注入法等に代表されるP VD法によって行うことができる。これらの中、アーク イオンプレーティング法の内容を説明すると、カソード を蒸発源とするアーク放電によってイオン化した金属成 分をN₂、CH₄ 又はBF₃ガス或いはそれらの混合ガスの雰 囲気中で反応させ、バイアス電圧を付与した基材表面に デポジットさせる。このとき、カソードとしてはAIとC r、AlとV、又は、AlとMgをそれぞれ個別に使用しても よいが、目的組成そのものからなる Ali-, X, をカソー ド(ターゲット)とすれば、皮膜組成のコントロールが 容易であるという利点がある。この場合、 Al_{1-y} X_y の 蒸発は数十アンペア以上の大電流域で行われ、そのため カソード物質(Al_{1-y}X_y)の組成ずれは殆ど生じず、 しかもイオン化効率が高くて反応性に富み、基材にバイ アス電圧を印加することによって密着性の優れた皮膜を 得られる。

[0023]

【実施例】

装置を用い、そのカソード電極として $Al_{1-y}X_y$ (但し、X: Cr, V又はMg, y:種々変化)のターゲットを取り付け、一方、該装置の基板(基材)ホルダーに基材として超硬合金(WC-10%Co系焼結合金)製の工具チップを取り付けた。又、該装置には、皮膜形成状態の均一性を確保するための基板回転機構及びヒータを設けた。【0024】そして、上記ヒータによって基材(チップ)を400 Cに加熱保持した状態で基材に-30Vのバイアス電圧を印加し、装置内に高純度 N_2 ガス又は N_2 / CH_4 混合ガスを導入した上で 1×10^{-3} Torrの雰囲気とし、アーク放電を開始して基材表面に膜厚5 μ m の成膜を行った。このようにして得られた皮膜の組成を表 $1\sim2$ (N

(実施例1)カソードアーク方式イオンプレーティング

o.1~33、36~68) に示す。この中、No.1~27、36~62 のものは本発明の実施例に係る硬質皮膜であり、No.28 ~33、63~68は比較例に係る皮膜である。

【0025】更に、比較のため、カソード(ターゲット)に $Al_{1-y}Ti_y$ 又はTiを用い、かかる点を除き上記と同様の装置及U方法により、(Al,Ti)N皮膜及UTiN 皮膜を形成した。それら皮膜の組成を表 $1\sim2$ に示す (No.34,35,69,70)。

【0026】このようにして皮膜形成された工具チップを用いて、次の2種類の条件で切削試験を行った。その試験結果を表1~2に示す。

- ① 被削材: S45C、切削速度: 170m/min、送り速度: 0. 25mm/rev、切り込み: 1 mm、切削時間: 25分
- ② 被削材:SKD11、切削速度:150m/min、送り速度:0.2mm/rev 、切り込み:2mm、切削時間:25分

【0027】表1~2から明らかなように、比較例に係る皮膜を有する工具チップに比べて本発明の実施例に係る皮膜を有する工具チップは、いづれも逃げ面摩耗量

(摩耗幅:摩耗箇所の幅)及びすくい面摩耗深さが極めて少なく、耐摩耗性に非常に優れている。

【0028】(実施例2)皮膜の耐酸化性を調べるために基材として白金板を用い、基材表面に形成する皮膜の厚みを10μmとし、これらの点を除き実施例1と同様の同様の装置及び方法により、表3に示す組成の皮膜を形成した。この中、No.71~76のものは本発明の実施例に係る硬質皮膜であり、No.77~84は比較例に係る皮膜である。

【0029】このようにして皮膜形成された白金板について、その皮膜の耐酸化性を調べるため、熱天秤装置を用いて昇温範囲:室温~1200℃、昇温速度:10℃/min、雰囲気ガス:乾燥空気、雰囲気ガスの流量:150cc/minの条件で酸化試験を行った。そして、昇温過程で生じる急激な重量増加点での温度を酸化開始温度と定め、それを求めた。その結果を表3に示す。又、皮膜のビッカース硬度(荷重50g)を測定した。その結果を表3に併記して示す。

【0030】表3から明らかなように、比較例に係る皮膜はTiN 皮膜では約600 ℃で、(AI,Ti)N皮膜では約800 ℃で酸化が始まるのに対し、本発明の実施例に係る皮膜はいづれも酸化開始温度が高く、高温耐酸化性に優れている。

[0031]

【表1】

No	皮膜の組成	被削材	逃げ面 摩耗幅 (mm)	すくい面 摩耗深さ (μm)	備考
1 2 3 4 5 6 7 8 9	(Alo. s, Cro. 1)N (Alo. s, Cro. 2)N (Alo. 7, Cro. 3)N (Alo. 8, Cro. 2)B (Alo. 8, Cro. 2)C (Alo. 8, Cro. 2)NC (Alo. 8, Cro. 2)NB (Alo. 8, Cro. 2)BC (Alo. 8, Cro. 2)BC	\$45C	0. 05 0. 04 0. 05 0. 07 0. 06 0. 04 0. 07 0. 08 0. 06	656845633	
10 11 12 13 14 15 16 17 18	(Alo. 9, Vo. 1)N (Alo. 8, Vo. 2)N (Alo. 7, Vo. 3)N (Alo. 8, Vo. 2)B (Alo. 8, Vo. 2)C (Alo. 8, Vo. 2)NC (Alo. 8, Vo. 2)NB (Alo. 8, Vo. 2)BC (Alo. 8, Vo. 2)NCB	\$45C	0. 06 0. 05 0. 07 0. 05 0. 05 0. 04 0. 08 0. 04 0. 03	767655874	本発明例
19 20 21 22 23 24 25 26 27	(Alo. 9. Mgo. 1)N (Alo. 9. Mgo. 2)N (Alo. 7. Mgo. 3)N (Alo. 9. Mgo. 1)B (Alo. 9. Mgo. 1)C (Alo. 9. Mgo. 1)NC (Alo. 9. Mgo. 1)NB (Alo. 9. Mgo. 1)BC (Alo. 9. Mgo. 1)NCB	\$45C	0. 05 0. 06 0. 07 0. 08 0. 06 0. 05 0. 07 0. 06 0. 04	67 89 85 67 4	
28 29 30 31 32 33	(Alo. 6, Cro. 4)N (Alo. 4, Cro. 6)N (Alo. 6, Vo. 4)N (Alo. 4, Vo. 6)N (Alo. 6, Mgo. 4)N (Alo. 4, Mgo. 6)N	S45C	0. 16 0. 17 0. 17 0. 18 0. 19 0. 20	1 9 2 1 2 2 2 3 2 5 2 6	比較例
34	TiN	S45C	0. 15	1 8	Licht/IRI
35	(Alo. s. Tio. 4)N	S45C	0.10	1 2	比較例

[0032]

【表2】

No	皮膜の組成	被削材	逃げ面 摩耗幅 (mm)	すくい面 摩耗深さ (µm)	備考
36 37 38 39 40 41 42 43 44	(Alo. 9, Cro. 1)N (Alo. 8, Cro. 2)N (Alo. 7, Cro. 2)N (Alo. 8, Cro. 2)B (Alo. 8, Cro. 2)C (Alo. 8, Cro. 2)NC (Alo. 8, Cro. 2)NB (Alo. 8, Cro. 2)BC (Alo. 8, Cro. 2)NCB	SKD11	0. 3 0 0. 25 0. 3 0 0. 25 0. 2 0 0. 2 5 0. 1 5	8 7 8 9 8 6 7 9 7	
45 46 47 48 49 50 51 62 53	(Alo. 8, Vo. 1)N (Alo. 8, Vo. 2)N (Alo. 7, Vo. 3)N (Alo. 8, Vo. 2)B (Alo. 8, Vo. 2)C (Alo. 8, Vo. 2)NC (Alo. 8, Vo. 2)NB (Alo. 8, Vo. 2)BC (Alo. 8, Vo. 2)NCB	SKD11	0. 3 0 0. 2 5 0. 3 0 0. 3 5 0. 2 0 0. 2 5 0. 1 5	9 8 1 0 1 1 1 0 7 9 8 6	本発明例
54 55 56 57 58 59 60 61 62	(Alo. 9. Mgo. 1)N (Alo. 8. Mgo. 2)N (Alo. 7. Mgo. 3)N (Alo. 9. Mgo. 1)B (Alo. 9. Mgo. 1)C (Alo. 9. Mgo. 1)NC (Alo. 9. Mgo. 1)NB (Alo. 9. Mgo. 1)BC (Alo. 9. Mgo. 1)NCB	SKD11	0. 20 0. 20 0. 30 0. 35 0. 25 0. 25 0. 20	8 9 1 0 9 9 7 8 9 6	
63 64 65 66 67 68	(Alo. 6, Cro. 4)N (Alo. 4, Cro. 6)N (Alo. 6, Vo. 4)N (Alo. 4, Vo. 6)N (Alo. 6, Mgo. 4)N (Alo. 4, Mgo. 6)N	SKD11	0. 65 0. 70 0. 70 0. 75 0. 80 0. 85	2 6 2 7 2 8 2 9 2 9 3 0	比較例
69	TiN	SKD11	0.60	2 5	比較例
70	(Al. Ti) N	SKD11	0.40	1 8	

[0033]

【表3】

No	皮膜の組成	酸化開始 温度 (°C)	ビッカース 硬度 (Hv)	備考
71 72 73 74 75 76	(Alo. s. Cro. 2)N (Alo. s. Vo. 2)N (Alo. s. Mgo. 1)N (Alo. s. Cro. 2)NC (Alo. s. Vo. 2)NB (Alo. s. Mgo. 2)BC	1 0 5 0 1 0 0 0 1 0 0 0 9 5 0 9 0 0 9 0 0	3 2 0 0 3 0 0 0 2 8 0 0 3 5 0 0 3 1 0 0 3 2 0 0	本発明例
77 78 79 80 81 82	(Alo. 6, Cro. 4)N (Alo. 6, Vo. 4)N (Alo. 6, Mgo. 4)N (Alo. 6, Cro. 4)NC (Alo. 6, Vo. 4)NB (Alo. 6, Mgo. 4)BC	7 0 0 6 5 0 6 5 0 5 5 0 6 0 0	2 1 0 0 1 8 0 0 1 5 0 0 2 2 0 0 2 0 0 0 1 9 0 0	比較例
83	TiN	600	2000	
84	(Al. Ti) N	8 0 0	2500	比較例

[0034]

【発明の効果】本発明に係る硬質皮膜は、耐熱性(高温耐酸化性)に優れ、又、硬度が高く、そのため、従来のTiN 皮膜、TiC 皮膜、TiCN皮膜、(Al,Ti)(N,C)系皮膜の中で最も耐摩耗性に優れている(Al,Ti)(N,C)系皮膜よりも耐摩耗性に優れ、高速切削の場合に対応可能な耐摩耗性を有し、従って、高速切削用工具基材の硬質皮膜とし

て好適に用いることができ、切削速度の一層の高速化が 図れるようになり、又、穿孔加工等の加工に使用される 工具や金型の耐摩耗性硬質皮膜として好適に用いること ができ、それらの耐摩耗性の向上による工具性能や金型 性能の向上及び寿命の向上が図れるようになるという効 果を奏する。

フロントページの続き

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